



Rapid removal of selenate in a zero-valent iron/ $\text{Fe}_3\text{O}_4/\text{Fe}^{2+}$ synergetic system



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ARTICLE INFO

Article history:

Received 16 August 2015

Received in revised form

29 November 2015

Accepted 30 November 2015

Available online 2 December 2015

Keywords:

Zero-valent iron

Selenate

Magnetite

Hybrid system

Synergetic effect

ABSTRACT

Batch experiments were conducted to investigate selenate reduction in a hybridized zero-valent iron (ZVI or Fe^0) system that was easily created by mixing magnetite and Fe^{2+} with ZVI particle (20 mesh) and preconditioning for 24 h prior to selenate addition. The performance of the hybrid ZVI/ $\text{Fe}_3\text{O}_4/\text{Fe}^{2+}$ system (hZVI) were compared with those of non-hybrid (ZVI, Fe^{2+} and Fe_3O_4 alone) or partial-hybrid systems (ZVI/ Fe^{2+} , $\text{Fe}_3\text{O}_4/\text{Fe}^{2+}$ and ZVI/ Fe_3O_4). The results showed that precondition of 24 h significantly increased the reactivity of hZVI towards selenate reduction possible due to the formation of reactive interface between ZVI and magnetite. hZVI achieved the most effective selenate removal than any of other systems. ZVI/ $\text{Fe}_3\text{O}_4/\text{Fe}^{2+}$ was a synergetic system, in which any constituent was indispensable for rapid removal of selenate. ZVI was the primary electron donor for selenate reduction. Fe^{2+} instead of acidic pH (H^+) participated in selenate reduction together with ZVI. Moreover, Fe^{2+} rejuvenated the passivated surface of ZVI and magnetite, and thus sustained the reactivity of hZVI for rapid removal of selenate. Magnetite served as the primary reaction sites for selenate removal. Se speciation extraction and X-ray photoelectron spectroscopy evidences indicated stepwise reduction of Se^{VI} to Se^{IV} and then to Se^0 or $\text{Se}^{-\text{II}}$ in the hZVI system. Findings of this study could help develop an hZVI technology suitable for treating various selenium-contaminated wastewaters.

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1. Introduction

Selenium (Se), an essential trace nutrient for many living organisms including humans, is toxic at elevated level [1]. Anthropogenic activities such as mining, smelting, oil refineries, coal-fired power plants, and agriculture runoff are the predominant sources in the natural aquatic environment [2,3]. For the common pH and redox conditions of most soil and aquatic environments, Se^{IV} and Se^{VI} are the dominant forms [4]. Selenite tends to adsorb onto soil minerals, particularly onto iron/aluminum-containing minerals [5,6], both of which are very abundant in the Earth. Selenate; however, a highly

soluble and chemically stable compound with higher bioavailability, exhibits only a weak adsorption affinity to most solid surfaces and attenuates slowly in the environment [2,7].

Multiple technologies have been explored for the remediation of Se-contaminated water and wastewater. Adsorption, coagulation, membrane filtration, ion exchange, biological and chemical reduction are all the methods currently used [1,3]. But high operating and maintenance costs for adsorption, coagulation, ion exchange and membrane filtration limit their wide application. Biological technology is a promising technology for Se contamination remediation, but its potential formation of highly toxic organic Se from biological treatment remains a concern [8].

Among the various chemical reduction technologies, zero-valent iron (ZVI) based technology is a promising approach due to its relatively low cost and toxicity [9,10]. It has been widely used for *in-situ* and *ex-situ* remediation of various organic and inorganic

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contaminants [11,12]. ZVI was capable of removing selenate from water via reduction, co-precipitation and adsorption [10]. However, the practicability of the process is markedly diminished by the iron surface passivation problem, and then fast loses its reactivity. In order to reduce or inhibit ZVI surface passivation and thus enhance ZVI reactivity and longevity, some additives were added to form a combined system, for example bicomponent system such as ZVI/sand [13], ZVI/ Fe_2O_3 [14], ZVI/activated carbon [15], ZVI/ MnO_2 [16] and ZVI/ Fe_3O_4 [17,18], triple component system such as ZVI/ Fe_2O_3 / Fe^{2+} [19] and ZVI/ Fe_3O_4 /graphene [20]. All of these additives could enhance ZVI reactivity in some degree towards specific contaminant removal. Among all the additives, Fe_3O_4 , a semiconductor with special electrical property, and Fe^{2+} are corrosive products from ZVI, both of which are reactive species in ZVI system [21]. Magnetite (Fe_3O_4) alone has a limited capacity for selenate adsorption [22] or for selenite redox reduction [23]. Surface-bound Fe^{II} was found to be effective for reductive removal of selenite [24], but it is not reactive for selenate reduction.

The strategy of augmenting a ZVI system with externally-supplied Fe^{2+} to overcome ZVI surface passivation was highly effective for trichloroethylene degradation [25], nitrate [26] and selenate reduction [27] by ZVI. The primary role of Fe^{2+} was to facilitate ferric (hydr) oxides, the passive corrosion products, transformation to magnetite, and thus enhanced selenate reduction by ZVI [27]. Similar to Fe^{2+} , other transition metals such as Mn^{2+} and Co^{2+} also enhanced selenate removal by ZVI [28]. As an electron-conducting iron oxide, magnetite can mediate redox reactions between ZVI and pollutants [18]. The previous study concluded that both Fe^{2+} and Fe_3O_4 are very important for pollutants degradation by ZVI [26], but they did not demonstrate ZVI/ Fe_3O_4 / Fe^{2+} as an integral system by strictly controlled experiments. Moreover, our studies showed ZVI/ Fe_3O_4 / Fe^{2+} hybrid system exhibited highly effective performance for heavy metals and nitrate reduction [29,30].

Based on the understanding of the important roles of Fe^{2+} and magnetite in overcoming ZVI surface passivation and sustaining ZVI system's reactivity for contaminants reduction, we hypothesized that introducing a separate magnetite phase into a ZVI/ Fe^{2+} system to form a hybridized ZVI/ Fe_3O_4 / Fe^{2+} system could further enhance the system reactivity for contaminant degradation such as selenate reduction. The objectives of this study were (1) to evaluate the efficiency of the hZVI system for selenate removal in comparison with non-hybrid systems; and (2) to provide some basic understandings on the roles of magnetite and Fe^{2+} as well as selenate reduction mechanisms in the hZVI system through carefully controlled batch tests and spectroscopic evidences.

2. Materials and methods

2.1. Materials

All chemicals used were analytical reagent grade. All reagent solutions were prepared with deoxygenated deionized (DDI) water (E-pure D4641, USA) and stored in an anaerobic chamber containing an atmosphere of 95% N_2 /5% H_2 with catalytic oxygen gas removal system (Coy Laboratory, USA). The DDI water was made by N_2 (>99.99%) bubbling for 1 h to remove dissolved oxygen, followed by stabilizing 72 h in the anaerobic chamber before use to remove DO completely. Stock solutions of SeO_4^{2-} and Fe^{2+} were prepared with Na_2SeO_4 (>99.8%, Johnson Matthey) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (J.T. Baker), respectively. Zero-valent iron grains of 20 mesh (>99.2%, Johnson Matthey) had a specific surface area of $0.073 \text{ m}^2/\text{g}$, which was measured by BET nitrogen absorption analysis (Autosorb-6, Quantachrome, USA). Magnetite powder (>95%) with a particle size

range of $0.1\text{--}0.5 \mu\text{m}$ and a specific surface area of $2.53 \text{ m}^2/\text{g}$ was purchased from Strem Chemicals, USA.

2.2. Batch experiments

During the preliminary experiment, unintentionally, we found that the precondition of ZVI- Fe_3O_4 - Fe^{2+} hybrid system prior to selenate addition could significantly increased hZVI reactivity towards selenate removal. Longer time duration precondition resulted in higher reactivity of hZVI. Thus, the effect of incubation duration on the reactivity of hZVI was investigated firstly.

Batch experiments were conducted using 12-mL serum bottles as reactors in the anaerobic chamber. In the preliminary test, the reactors, each pre-filled with $0.100 \pm 0.001 \text{ g}$ ZVI grain and $0.100 \pm 0.001 \text{ g}$ magnetite powder, were transferred into the anaerobic chamber, followed by adding with designed volumes of ferrous stock solution and DDI water up to 10 mL in total with a concentration of 0.5 mM Fe^{2+} , and then sealed with rubber stoppers and aluminum crimps. The reactors were then placed in a rotary tumbler for complete mixing at 30 rpm and room temperature ($21 \pm 2^\circ\text{C}$) in the dark for precondition. After preconditioning the hZVI system for 0, 2, 6, 12, 24 and 48 h, respectively, $50 \mu\text{L}$ selenate stock solutions was added into each reactor using a micro-syringe, resulting in 0.253 mM selenate (or 20 mg/L as Se) in 10.05 mL reactive mixture. At designed time interval, three reactors were withdrawn as triplicate for pH, dissolved selenate, selenite and Fe^{2+} determination after filtration through $0.2 \mu\text{m}$ membranes. The result of preliminary test showed that 24 h precondition duration was enough to activate the hZVI system. Thus, 24 h pretreatment time was chosen for further experiment to probe the effect of other parameters.

Same process as above was performed but just added various amount of Fe^{2+} and only pretreated 24 h prior to selenate addition. Moreover, six control experiments were conducted separately on non- or partial-hybrid systems of ZVI-only, Fe_3O_4 -only, Fe^{2+} -only, ZVI/ Fe_3O_4 , ZVI/ Fe^{2+} , and Fe_3O_4 / Fe^{2+} to compare with the hZVI system. All test results were reported as an average with a standard deviation bar from triplicate reactors.

To characterize the effect of precondition duration on the hZVI, the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ ratio of the suspended solid in the hZVI after precondition with different time was determined by chemical analysis because XRD could not distinguish the difference of microstructure of hZVI after preconditioning different time duration. Described as in the preliminary experiment mentioned above, a serial of reactors containing 10 g/L ZVI, $10 \text{ g/L Fe}_3\text{O}_4$, and 0.5 mM Fe^{2+} were incubated 0, 2, 6, 12, 24 and 48 h. After pretreatment, three reactors as triplicate were transferred to the anaerobic chamber before open the cover. After settling 2–3 min, a small amount of surface suspension ($\sim 0.5 \text{ mL}$) was gently collected by syringe to avoid collecting iron particles. Only some small size of corrosion products and magnetite were suspending after settling 2–3 min. They settled very slowly. The solid was retained on a filter membrane by filtration and rinsed with $5 \text{ mL } 0.2 \text{ M}$ acetic acid to remove surface-bound Fe^{2+} , followed by rinsing three times with DDI to remove residual acetic acid. Then the membrane together with the solid was placed in a new reactor and transferred to the anaerobic chamber quickly, followed by adding $10 \text{ mL } 3 \text{ M}$ deoxygenated HCl to dissolve the solid for Fe^{2+} and total iron determination after filtration.

Sequential dosing tests were performed to assess the role of dissolved Fe^{2+} in the hZVI system and the reusability of hZVI for selenate removal. Some procedure was described in previous study [27]. Another dose of selenate and Fe^{2+} were added once they were exhausted. When dissolved Fe^{2+} was exhausted, the reactors were split into three groups for three parallel tests: (1) the first group was augmented with 0.50 mM Fe^{2+} ; (2) the second group with 1.0 mM

HCl; and (3) the third group, as a control, without adding Fe^{2+} or HCl.

A sequential extraction experiment was performed to probe the Se speciation distribution during the reaction. Batch reactors were carried out with the initial condition controlled as 10 g/L ZVI + 10 g/L Fe_3O_4 + 0.50 mM Fe^{2+} + 0.253 mM selenate and a total volume of 10 mL. The following procedure was the same as showed in previous study [27].

2.3. Analytical methods

Dissolved selenite and selenate in filtrate were determined using a Dionex DX-500 ion chromatography (IC) on an IonPac AS-22 column using a CD-20 conductivity detector. The minimum detection limit of the IC method for both selenate and selenite was 20 $\mu\text{g/L}$ as Se (or 0.253 μM). Se in the NaOH, HCl, or HNO_3 extractions was measured using a hydride generation atomic absorption spectrometer (HG-AAS) (AAnalyst 400, PerkinElmer). Selenite was analyzed directly by the HG-AAS method. For the total Se, the filtrate sample was mixed with 12 M HCl at 1:1 volume ratio and pretreated in a boiling water bath for 30 min to reduce selenate to selenite before analysis. Selenate was calculated as the difference between the total Se and selenite. The HG-AAS method had a minimum detection limit of 1 ppb for Se. Dissolved Fe^{2+} was determined with the 1,10-phenanthroline method at 510 nm [31] on a UV-vis spectrophotometer (T80, PG Instruments). The total iron was determined by atomic absorption spectrometer (AAnalyst 400, PerkinElmer).

2.4. Material spectroscopic characterization

Powder X-ray diffraction (XRD) was used to characterize iron oxides morphology. Selected batch tests were repeated at designed reaction times, the reactors were sonicated to strip off iron corrosion scales and the resultant suspension (excluding the ZVI grains that settled at the bottom) was filtered to retain the iron oxide particles as a thin cake on the filter membrane. After rinsed with DDI water, the membrane with the iron oxide sample was dried by N_2 flushing and stored in an anaerobic chamber before analysis using a Bruker D8 powder X-ray diffractometer equipped with a monochromatized $\text{Cu K}\alpha$ radiation.

X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra Imaging) was used to determine the oxidation state of Se in the solid samples collected from the hZVI system. Samples were prepared similarly to the XRD sample preparation and analyzed with a monochromatized Al $\text{K}\alpha$ X-ray. The pressure in the analysis chamber was $1.33 \times (10^{-6} - 10^{-7})$ Pa. The charge neutralizer was used during all analysis to control the surface charging of samples. Pass energy of 40 eV and a step size of 0.1 eV were used to obtain the high resolution spectra. The binding energy was calibrated by assigning the C 1s peak to 284.5 eV. The peaks were integrated with Shirley background using PEAK 41 software.

3. Results and discussion

3.1. Effect of precondition on hZVI reactivity

The results of selenate removal and $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ ratio variation in the suspended solid after precondition are shown in Fig. 1. It indicates that precondition of $\text{ZVI}/\text{Fe}_3\text{O}_4/\text{Fe}^{2+}$ significantly increased selenate removal (Fig. 1a). It took about 7.5 h to remove added selenate in the hZVI system without precondition. And it shorten to 4.5 h, 2.5 h, 2.0 h and 1.5 h to immobilize added selenate after precondition of 2 h, 6 h, 12 h and 24 h, respectively. However, insignificant enhancement was observed when it was preconditioned 48 h.

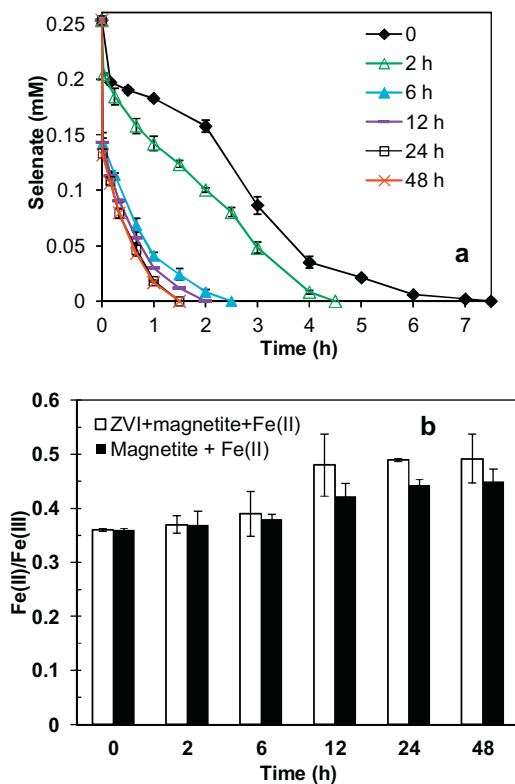


Fig. 1. Effect of precondition time duration on the (a) selenate removal and (b) $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ in the suspended solid in the hZVI system.

Similar result was obtained even after precondition 72 h (data not shown). It implied that some reactive species produced during precondition. This process was possible associated with surface adsorption, because it reached saturation after certain time and no enhancement was obtained. Previous studies also found that some highly reactive species were formed at the interface of Fe^0 and Fe_3O_4 after mechanical grinding and thermal reduction treatment [32,33]. But very low reactivity of $\text{Fe}^0/\text{Fe}_2\text{O}_3$ and Fe^0/FeOOH were observed, which implied that Fe_3O_4 was a key component for Fe^0/FeO_x combined system. The role of Fe^{II} was discussed in detail in Section 3.3. Moreover, XRD was employed to characterize the difference of hZVI microstructure after precondition. But due to the overlapping of added magnetite, no other peaks were detected in XRD spectrum (data not shown). In addition, SEM was performed to probe the morphology evolution before and after precondition (Fig. S1). The raw ZVI surface was smooth and irregular. Some small holes and pits were observed on the surface of ZVI. Raw magnetite powder was uniform in size (Fig. S1C). ZVI surface was almost covered by magnetite after precondition (Fig. S1B). But insignificant variation of magnetite surface morphology was obtained after precondition (Fig. S1D). Accordingly, chemical analysis of $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ ratio in the suspension of $\text{ZVI}/\text{Fe}_3\text{O}_4/\text{Fe}^{2+}$ and $\text{Fe}_3\text{O}_4/\text{Fe}^{2+}$ was conducted. As shown in Fig. 1b, the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ in the raw magnetite was only 0.36, not the stoichiometric 0.5, which suggested that it was partially oxidized by oxygen in the top air of the bottle during storage. Previous study also showed that magnetite would be slowly oxidized to $\gamma\text{-Fe}_2\text{O}_3$ by air in the bottle during storage at normal temperature [34]. But the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ ratio in $\text{ZVI}/\text{Fe}_3\text{O}_4/\text{Fe}^{2+}$ system gradually increased to 0.37, 0.39, 0.48, 0.49 and 0.492 after precondition of 2 h, 6 h, 12 h, 24 h and 48 h, respectively. Higher Fe^{II} proportion enhanced selenate removal. Although it was also increased in $\text{Fe}_3\text{O}_4/\text{Fe}^{2+}$ system from 0.36 to 0.37, 0.38, 0.422, 0.443 and 0.45 after precondition, they were all below that in hZVI system at the corresponding time duration.

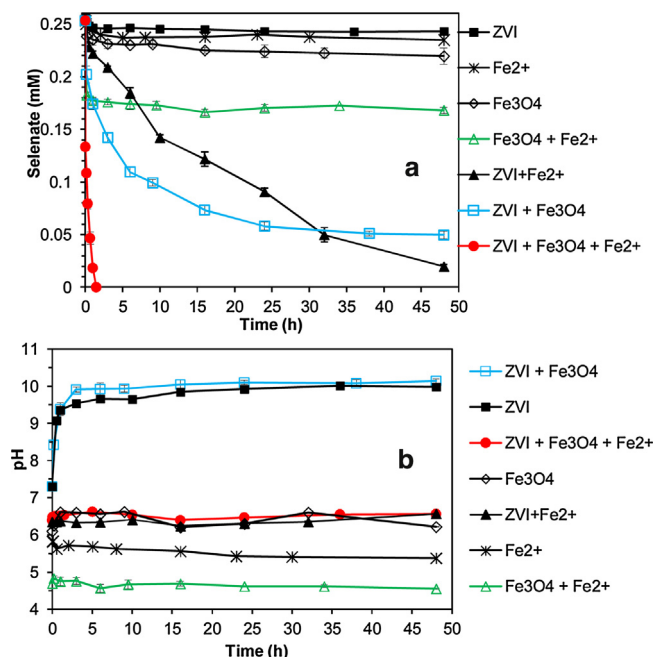


Fig. 2. Concentration profiles of (a) selenate and (b) pH in the seven treatment systems with different combinations of 10 g/L ZVI, 10 g/L Fe₃O₄, and 0.50 mM Fe²⁺. All systems were preconditioned for 24 h before adding 0.253 mM selenate at $t = 0$.

Previous study showed that the adsorption of Fe²⁺ onto magnetite was accompanied by the reduction of the octahedral Fe^{III} atoms in the underlying magnetite to octahedral Fe^{II} atoms, which transferred the partly oxidized magnetite to be more stoichiometric and thus enhanced the redox capability of magnetite towards contaminants [35,36]. The increase of Fe^{II}/Fe^{III} after precondition in this study might be the same the reason. But besides this occurrence, higher Fe^{II}/Fe^{III} ratio in ZVI/Fe₃O₄/Fe²⁺ system might result from some Fe^{II}-rich corrosion products released from Fe⁰ surface due to mechanical agitation. The difference of selenate removal in both systems would discuss in next section. The Fe^{II}/Fe^{III} in the suspended solid of ZVI/Fe₃O₄ was very low (0.37–0.39) and irregular after precondition (data not shown).

3.2. Selenate removal in different systems

Selenate removal in different systems is illustrated in Fig. 2. As shown, selenate removal rate varied greatly among different systems. The hybrid ZVI/Fe₃O₄/Fe²⁺ system exhibited the highest reactivity for selenate removal, achieving a removal of 0.253 mM selenate to below the detection limit within 1.5 h. Dissolved Fe²⁺ decreased coupled with selenate removal, and kept stable when selenate was removed (Fig. S2). It indicates that selenate removal would consume Fe²⁺ directly or indirectly. More interestingly, the pH remained largely stable at ~6.5 during the whole reaction duration, which implied that the hZVI system could buffer pH. Such pH could reduce ZVI dissolution compared to acidic condition in conventional ZVI technology [12]. In the ZVI/Fe²⁺ system, selenate decreased with a much slower rate, and ~8% selenate still remained after 48 h; though the pH profile during the test was similar to that of the ZVI/Fe₃O₄/Fe²⁺ system. Similar to ZVI/Fe₃O₄/Fe²⁺ system, the dissolved Fe²⁺ decreased coupling with selenate removal (Fig. S2). The result demonstrated that magnetite played an important role in accelerating selenate removal in the hybrid ZVI/Fe₃O₄/Fe²⁺ system. Faster selenate removal was observed after a black film coating (i.e., magnetite) forming on the surface of iron [27]. Similar role of magnetite was also observed during nitrate reduction by ZVI in the presence of Fe²⁺ [26]. In the ZVI/Fe₃O₄ system (without

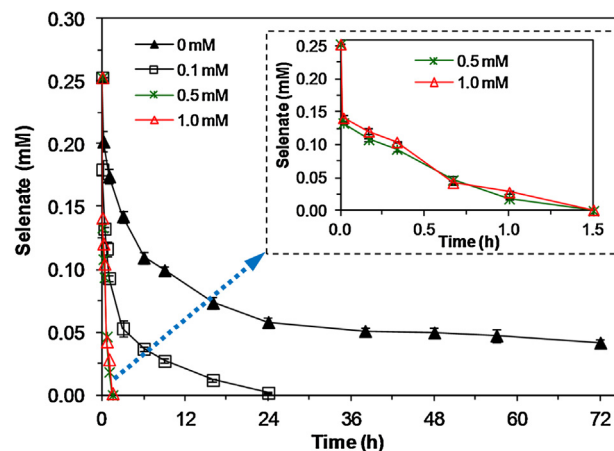


Fig. 3. Effect of Fe²⁺ and magnetite dosage on selenate removal in the ZVI/Fe₃O₄/Fe²⁺ system. The initial experimental condition was controlled as 10 g/L ZVI + 10 g/L Fe₃O₄ + varied Fe²⁺ (0, 0.1, 0.5, 1.0 mM) with 24 h precondition + 0.253 mM selenate.

Fe²⁺ augmentation), selenate was removed at the second fastest rate in the first 24 h, but little decrease was observed after 24 h. In this system, pH increased rapidly to 10 in 3 h and remained stable afterwards. The high pH might contribute in part to the passivation of ZVI surface so that Se^{VI} removal was inhibited [37], but the absence of Fe²⁺ due to high pH was the more probable reason. Initial fast removal of Cr(VI) coupled with pH increase and then it inhibited Cr(VI) removal by ZVI/Fe₃O₄ was observed in a previous study, but it resumed fast removal of Cr(VI) after addition of acid coupled with Fe²⁺ release [17]. The important role of Fe²⁺ for contaminants removal by ZVI has also been proved in previous studies [25,27]. As discussed in Section 3.1, the Fe^{II}/Fe^{III} ratio in the suspended solid of ZVI/Fe₃O₄ was low (0.37–0.39). But its high reactivity towards selenate might be due to the formation of reactive interface between ZVI and Fe₃O₄ after precondition, because these reactive species were excluded during preparing sample for Fe^{II}/Fe^{III} determination. Highly reactive species in the interface of ZVI/Fe₃O₄ was formed after mechanical grinding [33]. In the Fe₃O₄/Fe²⁺ system and the Fe₃O₄-only system, selenate decreased quickly by 27% and 6%, respectively, in the first 10 min but stayed unchanged afterwards. The poorer removal efficiency in the Fe₃O₄-only system (with pH 6.5) comparing to the Fe₃O₄/Fe²⁺ system (pH 4.7) was probably caused by the different pH, because selenate sorption onto magnetite decreased with increasing pH [22]. The lowest removal efficiency (~4%) was observed in the ZVI-only system due to ZVI surface passivation quickly. Similar to ZVI-only, Fe²⁺-only system only achieved ~5% removal. Most of Fe²⁺ (>90%) kept dissolvable in the whole reaction period (Fig. S2). These results demonstrated that ZVI, Fe₃O₄ and Fe²⁺ alone or partly hybridized system only achieved limited efficiency for selenate removal. Only when the three constituents together could it achieve the best removal efficiency of selenate. It suggested that the hZVI is a synergetic system. Any of constituent is indispensable. The interaction among them contributed to rapid removal of selenate.

3.3. The role of Fe²⁺ in the hZVI system

Fig. 3 shows that the addition of Fe²⁺ into ZVI/Fe₃O₄ system significantly increased selenate removal rate. In the absence of Fe²⁺, selenate removal in the ZVI/Fe₃O₄ system could not sustain and still remained ~20% even after 72 h. When 0.10 mM Fe²⁺ was externally-supplied, selenate removal was significantly promoted and it only took 24 h to remove the added selenate to below the detection limit. The added Fe²⁺ was consumed quickly (Fig. S3).

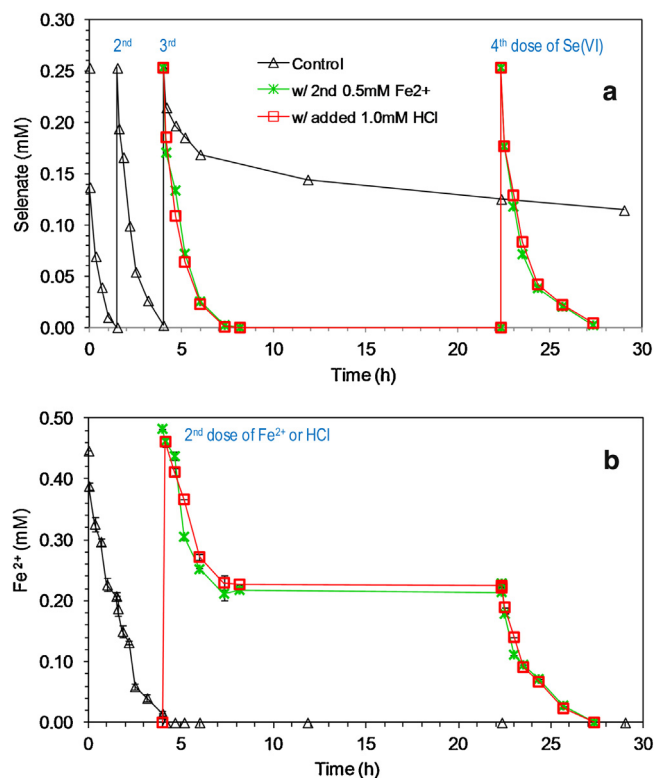
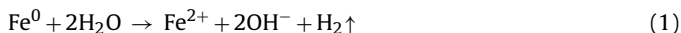


Fig. 4. Concentration profiles of (a) dissolved selenate, and (b) dissolved Fe^{2+} in the sequential dosing experiment. The reactors started with 10 g/L ZVI + 10 g/L Fe_3O_4 + 0.50 mM Fe^{2+} (24 h precondition) + 0.253 mM selenate (1st dose). The 2nd dose of 0.253 mM selenate was added at $t = 1.5$ h. The 3rd dose of 0.253 mM selenate was added at $t = 4$ h in three ways: (1) together with a new dose of 0.50 mM Fe^{2+} ; (2) together with 1.0 mM HCl; or (3) alone without additional Fe^{2+} or HCl as the control. The 4th dose of 0.253 mM selenate was added at $t = 22$ h.

When the Fe^{2+} dosage increased to 0.50 mM, the time required for selenate removal was shortened to 1.5 h. The added Fe^{2+} decreased gradually along with selenate removal. About 0.25 mM Fe^{2+} was consumed (Fig. S3). A further increase of Fe^{2+} dosage to 1.0 mM; however, negligible improvement was observed. Similarly, the Fe^{2+} decreased (~ 0.28 mM) coupling with selenate removal (Fig. S3).

The results demonstrated the key role of Fe^{2+} in the hybrid system. Similar role of Fe^{2+} towards selenate removal by ZVI was also observed in the anaerobic [27] and oxic condition [38]. In the absence of Fe^{2+} , the continued ZVI anoxic corrosion with water as an oxidant (Eq. (1)) could result in a steady increase of pH from near neutral to above 9.0 coupling with Fe^{2+} release.



Such high pH and the buildup of FeO_x on ZVI surface could be detrimental to the reactivity of ZVI [21]. The kinetic rate constants for selenate removal in different systems were summarized in Table S1. The data fit well with pseudo-first order kinetic reaction. The rate constant increased with the increase of Fe^{2+} concentration. The removal rate was very low in the absence of Fe^{2+} ($k = 0.05$). But it dramatically increased to 0.75 and 2.54 when 0.1 mM and 0.5 mM Fe^{2+} was added, respectively. However, similar rate constant value was obtained in the presence of 1.0 mM Fe^{2+} . The highest rate constant for selenate removal by ZVI was only 1.122 under oxic condition and initial pH 4.0 [10]. It is more than twice in the hZVI system, which implied that hZVI is a high reactive system for selenate removal.

The role of Fe^{2+} for selenate removal in the hZVI system was further demonstrated in the sequential dosing experiment (Fig. 4). The results showed that dissolved Fe^{2+} decreased coupled with sele-

nate removal. The first dose of 0.253 mM selenate was removed in 1.5 h in the presence of abundant Fe^{2+} . Removal of the 2nd dose of 0.253 mM selenate was completed in 2.5 h. By that time, 0.5 mM Fe^{2+} initially added was nearly totally consumed. Some residual Fe^{2+} might still exist in the form of surface-bound Fe^{2+} on the magnetite and ZVI grain. The removal rate of the 3rd dose of selenate decreased dramatically without replenishing Fe^{2+} (the control).

The residual surface-bound Fe^{2+} might contribute to the partial removal of selenate after dissolved Fe^{2+} depleted. Like the ZVI/ Fe_3O_4 system in the absence of Fe^{2+} (Fig. 2a), similar mechanism for selenate removal might occur. When a new dose of 0.50 mM Fe^{2+} was introduced together with the 3rd dose of selenate, rapid selenate reduction resumed. Once selenate removal completed, dissolved Fe^{2+} remained unchanged between $t = 7$ and 22 h until the 4th dose of selenate was injected. The results demonstrated that Fe^{2+} was very important for fast removal of selenate. This was consistent with the result obtained in Section 3.2. In order to prove the direct role of Fe^{2+} not acidic pH, HCl was added to the system when Fe^{2+} was depleted. A stoichiometric of 0.5 mM Fe^{2+} was released after 1.0 mM HCl was added. Interestingly, the system behaved similarly to that of directly adding 0.50 mM Fe^{2+} in term of selenate reduction, Fe^{2+} consumption, and pH variation. The result obviously suggested that Fe^{2+} instead of acidity (i.e., H^+) played the key role for rapid removal of selenate in the hZVI system. The promotion effect of Fe^{2+} on nitrate reduction by ZVI/ Fe_3O_4 was also reported [26]. Previous studies showed that limited aeration increased Fe^{2+} release and then enhanced selenate removal by ZVI, but excess aeration decreased removal rate due to oxidation of the released Fe^{2+} [10,37]. It is easily to understand that under limited aeration, the dissolved oxygen (DO) was deficient and the released Fe^{2+} from aerobic corrosion was available for selenate reduction and iron corrosion products transformation. But excessive aeration led to Fe^{2+} oxidation to ferric oxy-hydroxides by DO and covered on the surface of ZVI, which passivated ZVI surface and thus decreased selenate removal [37]. Moreover, a slight of yellow suspended solid was observed after one hour of reaction with selenate in ZVI- Fe^{2+} system in our previous study [27]. The yellow suspended solid was then gradually transferred to gray and then to black (i.e., magnetite). Moreover, ~ 0.50 mM Fe^{2+} was consumed for 0.50 mM selenate reduction. The stoichiometry between selenate and Fe^{2+} was $\sim 1:1$, which implied that Fe^{2+} also participated in selenate reduction by ZVI. It was consistent with selenate removal by ZVI/ Fe^{2+} system [27]. Therefore, it could be inferred that the Fe^{2+} not only participated in selenate reduction directly with ZVI, but also rejuvenated the surface of ZVI and the raw magnetite which had been partially-oxidized during storage, by transferring the passive coating to a reactive medium favoring electron transfer for selenate reduction.

3.4. Fate of Se in the hZVI system

Speciation distribution of Se in the ZVI/ Fe_3O_4 / Fe^{2+} system is illustrated in Fig. 5. As dissolved selenate decreased, the removed Se could be mostly recovered as adsorptive selenite and elemental Se extracted by NaOH and HNO_3 , respectively. More adsorptive selenite than selenate was obtained due to stronger bound of selenite onto magnetite, which was consistent with previous study [22]. No selenate or selenite was extracted by HCl, indicating no $\text{Fe}_2(\text{SeO}_4)_3$, $\text{Fe}_2(\text{SeO}_3)_3$ or FeSeO_3 precipitates were present. But the presence of $\text{FeSe}/\text{FeSe}_2$ was not clear, because they could escape as H_2Se gas during HCl extraction. In all reaction duration, no measurable selenite had ever been detected in aqueous phase, because selenite formed strong inner-sphere surface complexation with iron oxides [6,22]. Solid-bound selenate reached to a maximum of 11% of total Se (0.253 mM) at 1 h and then decreased slowly to 5% at 2 h. Solid-bound selenite accumulated rapidly, reaching 28% within the first

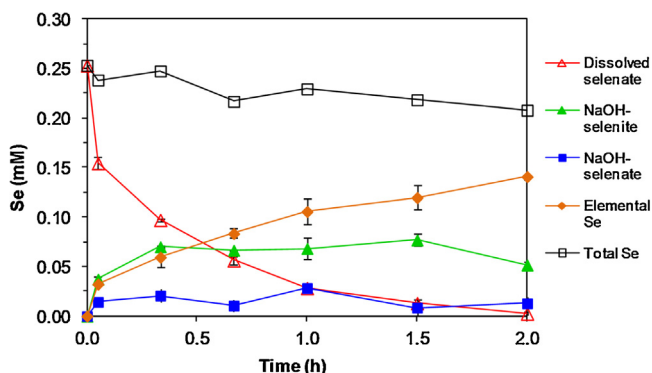


Fig. 5. Speciation distribution of selenium in the ZVI/Fe₃O₄/Fe²⁺ system. The initial experimental condition was controlled as 10 g/L ZVI + 10 g/L Fe₃O₄ + 0.50 mM Fe²⁺ (24 h precondition) + 0.253 mM selenate.

20 min before it leveled off and then decreased after 1.5 h. Elemental Se accumulated gradually, reaching 56% of total Se at 2 h. Elemental Se was also the main product from selenate reduction by ZVI under different condition [27,34,39], or selenite reduction by ZVI [40]. The incomplete recovery of total Se suggested the existence of other Se species such as selenide, which was volatilized during HCl extraction and confirmed by XPS analysis (Fig. 6). The binding energies of 164.5, 161.3 and 159.7 eV were assigned to Se^{IV}, Se⁰, and Se^{-II} or Se^{-I}, respectively, according to NIST X-ray Photoelectron spectroscopy database. Calculated by their peak area, about 55%, 40.7% and 4.3% of the added Se^{VI} were transformed to Se⁰, Se^{-II} or Se^{-I}, and adsorbed Se^{IV}, respectively, after 24 h reaction. FeSe and/or FeSe₂ were also observed during selenate reduction by ZVI under different conditions [9,10,27]. The pattern of Se distribution and evolution in hZVI system obtained by chemical and XPS analysis indicated that stepwise reduction of Se^{VI} to Se^{IV}, then to Se⁰ and even Se^{-I}/Se^{-II} was the main mechanism for selenate removal. Similar reduction pathway of selenate by ZVI had also been observed in a previous study [10,27].

3.5. Selenate removal mechanisms in different systems

3.5.1. Selenate removal in the non-hybrid and two components combined systems

The hZVI system comprises several sub-systems, such as ZVI-only, Fe₃O₄-only, Fe²⁺-only, ZVI/Fe²⁺, ZVI/Fe₃O₄, and Fe₃O₄/Fe²⁺ systems, all of which contribute to rapid removal of selenate.

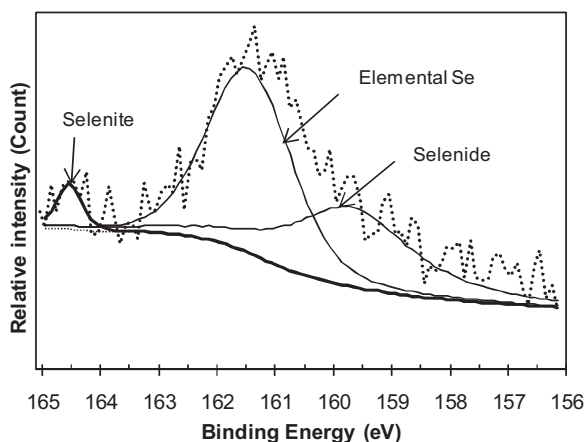
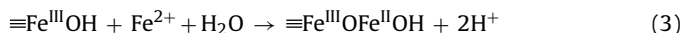
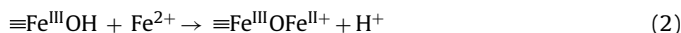


Fig. 6. XPS high resolution spectra of Se 3p_{3/2} on the iron oxide samples collected from the ZVI/Fe₃O₄/Fe²⁺ system with the experimental condition as: 10 g/L ZVI + 10 g/L Fe₃O₄ + 1.50 mM Fe²⁺ + 0.76 mM Se^{VI}.

The mechanisms of selenate removal varied in different systems. Therefore, we would separately discuss the mechanism of selenate removal in each system. The initially rapid but incomplete selenate decrease in the Fe₃O₄/Fe²⁺ system (Fig. 2a) suggested that adsorption instead of reduction was the most likely responsible for selenate removal. Selenate adsorption onto magnetite was facilitated by low pH (~4.7) [22]. Surface-bound Fe^{II} was only redox reactive for selenite but not for selenate as described in previous study [24]. In the Fe₃O₄-only system with higher pH (~6.5), much less selenate was adsorbed onto the magnetite. 0.50 mM Fe²⁺ solution would have a natural pH of ~6. The pH decrease after mixing of Fe²⁺ with magnetite probably resulted from Fe²⁺ adsorption reactions onto magnetite as following (Eqs. (2) and (3)) [41]. Dramatically decrease of dissolved Fe²⁺ was observed in the initial 10 min due to sorption onto Fe₃O₄ (Fig. S2). After that the Fe²⁺ and selenate almost kept stable (Figs. 2 and S2).



Moreover, Fe²⁺ adsorption onto Fe₃O₄ could increase the surface positive charge that favored selenate sorption [42].

In the ZVI/Fe₃O₄ system, a fast selenate removal was observed initially, accompanied with rapid pH increase to 10 in the first 3 h. The selenate removal; however, was not sustainable and after 24 h, the removal rate decreased to negligible (Fig. 2a). It was known that under non-acidic condition, ZVI surface could be rapidly passivated (especially at pH > 9) and thus rapidly lost its reactivity toward pollutants reduction [21]. In the ZVI/Fe₃O₄ system; however, the high pH (>10) did not immediately completely inhibit selenate removal. Compared with the ZVI-only system that had a similar pH but achieved negligible selenate removal, the presence of magnetite appeared to enhance significantly selenate removal. The exact mechanism and the role of magnetite were still unclear. Previous studies showed that mechanical alloying of ZVI and magnetite could produce a reactive interface (surface reactive Fe^{II}) that significantly accelerated chromate and H₂O₂ reduction [17,32,33]. Similarly, a mutual effect between ZVI and Fe₃O₄ was also proposed to explain the highly active nano ZVI/Fe₃O₄ for Cr(VI) removal [43]. Accordingly, we speculated that interactions between ZVI and magnetite during the 24 h preconditioning period prior to the addition of selenate might produce a reactive interface: e.g., electron from ZVI might be imparted to magnetite, forming of a Fe^{II}-enriched non-stoichiometric magnetite (just a thin interfacial layer) that was highly reactive for selenate reduction. After transferring electrons to selenate, the reactive Fe^{II}-bearing species was oxidized to a ferric oxide (e.g., Fe₂O₃) which would passivate the interface by blocking the pathway of electron transfer, and thus stop any further selenate reduction. XPS was performed to probe the Fe speciation on the surface of ZVI and magnetite after precondition in hZVI system (Fig. S4). Binding energy at 711.1 eV is the signal of magnetite. The peak shifts to lower binding energy suggesting more Fe(II) was present. No obvious Fe⁰ peak was detected on the surface of ZVI implying that the ZVI surface was covered by Fe(II)-rich compounds. Moreover, this hypothesis was also partially proved by the increase of Fe(II)/Fe(III) (Fig. 1b) in the preconditioned hZVI, and the fact that selenate reduction was slower in a freshly prepared ZVI/Fe₃O₄ system than that of experiencing 24 h precondition (Fig. S5).

The selenate removal mechanisms in the ZVI-only, Fe²⁺-only and ZVI/Fe²⁺ system were discussed in another study [27]. In brief, in the absence of Fe²⁺, ZVI surface was passivated rapidly with negligible selenate reduction under anaerobic condition; in a ZVI/Fe²⁺ system, selenate was reduced with magnetite as the iron corrosion product, which produced a hybrid system for sustainable selenate removal. Minor selenate removal was observed in the only presence of Fe²⁺ probably due to the precipitation of FeSeO₄. The synergistic

effect of ZVI and Fe^{2+} has also been observed during selenite [40] and nitrate [26] reduction by ZVI.

3.5.2. Selenate removal in the ZVI/ Fe_3O_4 / Fe^{2+} synergetic system

Among the all systems evaluated, the synergetic system of hZVI achieved the highest selenate removal efficiency. The hZVI system comprised several sub-systems as discussed above, all of which might occur in the hZVI system. Moreover, the synergetic effect among ZVI, Fe_3O_4 and Fe^{2+} might occur and some reactive species could be continuously produced for rapid removal of selenate. We proposed a complex process for selenate removal in the hZVI system as below. During the preconditioning, magnetite particles ($\sim 0.2\ \mu\text{m}$) attached to the ZVI grain surface or deposited in its pores and crevices to cover most of the ZVI surface. It could be proved by SEM image, which showed that most surface of ZVI was covered by magnetite (Fig. S1B). The magnetic property of magnetite facilitated the surface attachment of each other, and thus a reactive interface was produced as described in previous studies [32,33]. After addition of selenate to the preconditioned hZVI system, selenate was mostly adsorbed onto magnetite surface due to higher surface area and partly to ZVI surface firstly, followed by reduction. There were four possible pathways for selenate removal in hZVI system: (1) sorption onto magnetite and ZVI surface, especially magnetite; (2) direct reduction on the ZVI surface which has been pre-activated by Fe^{2+} during precondition [37]; (3) reduction by the Fe^{2+} -modified magnetite attached to the ZVI surface from which electron was [17]; and (4) reduction by the reactive interface produced in precondition between magnetite and ZVI (Fig. S6). All these pathways would contribute to selenate reduction in the hZVI system. Pathways (3) and (4) were likely the more important pathways for selenate removal based on the above results. The proposed roles of magnetite in pathways (3) and (4) was further corroborated in additional tests that showed that doubling the dosage of magnetite from 10 g/L to 20 g/L in an hZVI system would proportionally increase the overall selenate reduction rate (Fig. S7). It took 1.5 h to remove added selenate in the presence of 10 g/L magnetite in hZVI system. But it only took 0.9 h to remove same amount of selenate in the presence of 20 g/L magnetite. It implied that pathway (4) might be the most important contribution for rapid removal of selenate in the hybrid system. Therefore, the unique physicochemical properties of magnetite such as metallic-like electron conductivity, non-stoichiometric flexible composition ($\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ ratio), strong magnetic property, and the point of zero-charge at near neutral pH as well as the presence of substantial reactive surface-bound or structural Fe^{II} might facilitate the role(s) of both magnetite and Fe^{2+} in promoting the hZVI system reactivity. At the consumption ratio of approximately 1 mol Fe^{2+} per 1 mol Se^{VI} reduction to Se^{IV} or Se^0 , Fe^{2+} could not be the primary electron source, and therefore ZVI was also the electron source for Se species reduction. The main role of Fe^{2+} involved regulating the iron chemistry on the iron oxide–water interface to maintain the reactivity of ZVI and magnetite particles. Hence, the three key components, ZVI, Fe_3O_4 , and Fe^{2+} are all indispensable to the hZVI system. hZVI was a synergetic system.

4. Conclusions

In summary, this study demonstrated that the hybrid ZVI/ Fe_3O_4 / Fe^{2+} was a synergetic system. Any constituent in the hybrid system was indispensable, all of which contributed to rapidly removing selenate through various pathways. Precondition of hZVI produced some reactive interface between ZVI and magnetite assisted by Fe^{2+} and thus significantly promoted selenate removal in hZVI system. In this system, ZVI was the main electron donor for selenate reduction. Externally-supplied Fe^{2+} overcame

the passivation of ZVI and mediated the iron corrosion products transformation to magnetite as well as participation in selenate reduction together with ZVI. Magnetite served as reactive interface for selenate reduction, and semiconductor for electron transfer. Stepwise reduction of selenate to selenite, and to elemental Se and even selenide was the main pathway for Se^{VI} removal. The technology based on hZVI system is a promising approach for selenate removal from water and wastewater.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (21407091) and Talent Startup Fund of China Three Gorges University (0620130074). We also thank the anonymous reviewers for their comments on this manuscript.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2015.11.045>.

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